

# Statistical and Low Temperature Physics (PHYS393)

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## Required Background

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#### 1. Thermodynamics (PHYS253)

(Covers most of the basic ideas. It would help to look through the notes again.)

#### 2. Quantum and Atomic Physics (PHYS255)

(You need: Schrodinger's equation, particle in a box, simple harmonic oscillator, Zeeman effect, fermions and bosons.)

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### Recommended reading:

1. Statistical Mechanics - A Survival Guide,  
A. M. Glazer and J. S. Wark  
Oxford University Press, 2001
2. Basic Superfluids  
Tony Guenault  
Taylor & Francis Inc., 2003

Both available as ebook in the Liverpool University library.

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### Part 2: Superfluids and Superconductors

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6. Liquid Helium-4.
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## 1. Basic Statistical Mechanics

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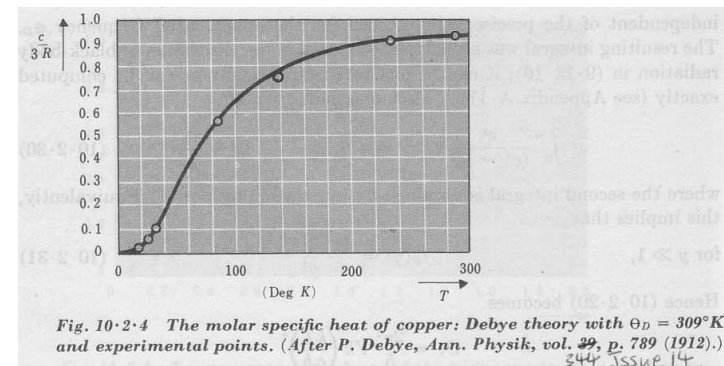
Thermodynamics, briefly.

1. Thermodynamics
2. Quantum mechanics
3. Statistical mechanics
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### Heat capacities

This graph shows the heat capacity of copper. At high temperatures ( $T$ ), it tends to a constant. At low  $T$ , it falls to zero.



The main theme in Part 1 is to learn how to explain such behaviours.

The study of heat engines in the 19th century led Rudolf Clausius to propose in 1822 the second law of thermodynamics in this form: "In a closed cycle, the sum of  $\delta Q/T$  is zero."

<http://en.wikipedia.org/wiki/Entropy>

$\delta Q$  is an infinitesimal heat change. Later,  $\delta Q/T$  came to be written as  $\delta S$ , or

$$dQ = TdS,$$

and  $S$  became known as the entropy.

Clausius statement implies that this abstract quantity  $S$  is a state function. E.g. if you compress and expand a gas and go back to the initial  $p$  and  $V$  at the end, then  $S$  also returns to the same value. (Note that  $Q$  itself is not a state function.)

### Quantum mechanics, briefly.

The chemical potential  $\mu$  is equal to the Gibbs free energy at equilibrium. The Gibbs free energy is

$$G = U + pV - TS.$$

One simple use of  $\mu$  is to find the energy change between two phases at constant  $p$  and  $T$ :

$$\Delta\mu = \Delta U + p\Delta V - T\Delta S.$$

At phase transition between liquid and gas, this would be the energy difference between 1 mole of liquid changing to gas, and 1 mole of gas changing to liquid at the same  $T$  and  $p$ . So

$$\Delta\mu = 0$$

gives the condition for phase equilibrium, because then there is no energy advantage in more liquid changing to gas, or the other way round.

[http://en.wikipedia.org/wiki/Gibbs\\_free\\_energy](http://en.wikipedia.org/wiki/Gibbs_free_energy)

This is the 1D Schrodinger's equation.

$$\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V(x)\psi = E\psi,$$

where  $m$  is the mass of a particle,  $\psi$  is the wavefunction,  $V(x)$  the potential it experiences, and  $E$  its energy.

In free space,  $V(x)$  would be zero. Solving the equation then gives

$$\psi = e^{ikx} \text{ or } e^{-ikx},$$

where  $k$  is related to  $E$  given by

$$E = \frac{\hbar^2 k^2}{2m}.$$

The Scrodinger's equation is based on the postulate for the momentum  $p_x$  of a particle:

$$-i\hbar \frac{d}{dx} = p_x.$$

We use this on a wavefunction  $\psi$  like this:

$$-i\hbar \frac{d\psi}{dx} = p_x \psi.$$

Applying this to the free space wavefunction  $e^{ikx}$ , we find

$$p_x = \hbar k.$$

## Statistical mechanics

In a 1D box of length  $L$ , the potential  $V(x)$  could be zero for  $x$  between 0 and  $L$ , and infinity otherwise.

This means that the wavefunction must be zero outside the box, and also zero at the "walls" at  $x$  equals 0 and  $L$ .

Inside the box, it is like free space, so  $\psi$  is  $e^{ikx}$  or  $e^{-ikx}$ . In order for  $\psi$  to be zero at the walls, these can be combined to give

$$\psi = \sin kx = \frac{e^{ikx} - e^{-ikx}}{2i}.$$

Applying the condition that this is zero at the walls, we find

$$k = \frac{n\pi}{L},$$

where  $n$  is an integer. This shows that the energy is quantised:

$$E = \frac{\hbar^2 k^2}{2m} = \frac{n^2 \pi^2 \hbar^2}{2mL^2}.$$

## Microstates

In quantum mechanics, energies are often quantised. We have seen that this happens for a particle in a box.

Consider a system with  $N$  particles. This could be atoms in a solid. For now, think of each one like a particle in a box.

Suppose every particle has energy levels  $\varepsilon_1, \varepsilon_2, \dots$

A microstate refers to a specific arrangement of particles among the energy levels, e.g. particle 1 in  $\varepsilon_3$ , particle 2 in  $\varepsilon_1$ , ...

A macrostate refers to a distribution of particles among the levels, e.g. 6 particles are in  $\varepsilon_1$ , 4 particles are in  $\varepsilon_2$ , ...

Suppose there are  $n_1$  particles in  $\varepsilon_1$ ,  $n_2$  particles in  $\varepsilon_2$ , ...

The macrostate can be written as  $(n_1, n_2, \dots)$ , or simply  $n_i$  where  $i = 1, 2, \dots$ . Then

$$N = n_1 + n_2 + \dots$$

Suppose the system is thermally isolated from the surrounding, so that the total energy  $E$  is constant.  $E$  is given by

$$E = n_1\varepsilon_1 + n_2\varepsilon_2 + \dots$$

These two equations impose constraints on the number of particles possible on each energy level.

### Constraints

Assuming the constraints

$$N = n_1 + n_2 + \dots$$

and

$$U = n_1\varepsilon_1 + n_2\varepsilon_2 + \dots$$

it is possible to solve for the most probably macrostate using the method of Lagrange multipliers.

Before that, we need to write down the number of possible microstates for a the macrostate. This is just the number of ways to arrange  $N$  different objects in some boxes, with  $n_1$  objects in box (level) 1,  $n_2$  objects in box 2, and so on.

Using the method of combinations, the number of arrangements is

$$\Omega = \frac{N!}{n_1!n_2!\dots}$$

The problem is to find the values of  $n_i$  that gives the largest  $\Omega$ .

More than one microstate can have the same macrostate. E.g. if the macrostate has 4 particles are in  $\varepsilon_2$ , then these 4 particles can be any of the  $N$  particles.

Basic postulate of statistical mechanics:

“A system is equally likely to be in any microstate that satisfies the constraints.”

This means that a system is most likely be be in the macrostate with the largest number of microstates. We may call this the most probably macrostate.

Using the method of statistics, it can be shown that if  $N$  is very large, then the probability of other macrostates is very close to zero. (E.g. when you take the average of more readings in an experimient, the error gets smaller.)

### Method of Lagrange multipliers.

The steps are as follows.

1. Write down the Lagrange function  $\ln \Omega + \lambda_1 N + \lambda_2 U$ . Two new variables,  $\lambda_1$  and  $\lambda_2$ , have to be introduced.
2. Differentiate with respect to each of  $n_i$  and  $\lambda_1$ ,  $\lambda_2$ .
3. Set all derivatives to zero. Solve the equations for  $n_i$ .

The answer is:

$$n_i = A \exp(\lambda_2 \varepsilon_i)$$

where  $A$  is  $\exp(\lambda_1)$ .

There are two unknowns  $A$  and  $\lambda_2$ . In principle, we can substitute into the above constraints and solve for these. Unfortunately, the equations are too complicated.

Around 1872, Ludwig Boltzmann postulated the connection between entropy  $S$  and the number of macrostates  $\Omega$ :

$$S = k_B \ln \Omega.$$

This formula allows us to use thermodynamics, e.g. using

$$dQ = TdS,$$

to find the answer to the most probable macrostate. Assuming Boltzmann's postulate, it can be shown that

$$\lambda_2 = -1/k_B T,$$

so that the distribution becomes

$$n_i = A \exp(-\varepsilon_i/k_B T).$$

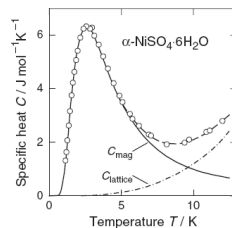
This is now called the Boltzmann distribution.

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### Paramagnetic salts.

Heat capacities tend to increase with temperature, as particles can reach higher energy levels.

At very low temperatures, paramagnetic magnetic shows a peak in its heat capacity.



J.W. Stout, W.B. Hadley, J. Chem. Phys. 40, 55 (1964)

This unusual behaviour is called the Schottky anomaly.

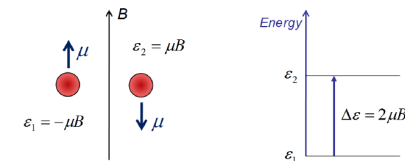
### Paramagnetic salts

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### Schottky anomaly

The Schottky anomaly happens for paramagnetic materials in a magnetic field. At very low temperatures, there is little contribution from electrons and phonons (lattice vibration).

Consider a material with ions that have spin 1/2. This is called a spin 1/2 paramagnet. When a magnetic field  $B$  is applied, the energy level of each ion split into two.

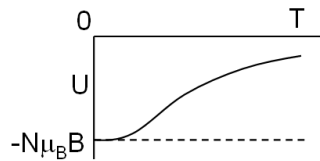


The energy levels are

$$\varepsilon = -\mu \cdot \mathbf{B} = -\mu_B B \text{ or } +\mu_B B$$

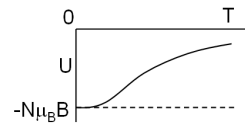
Lets see if we can “deduce” the Schottky anomaly. At 0 K, all electrons are at the ground state, so the total energy  $U$  is  $-N\mu_B B$ , where  $N$  is the number of the ions.

At high temperatures, the thermal energy the electrons is much larger than the difference between the two magnetic energy levels. Then the electrons are equally likely to be in  $-\mu_B B$  or  $+\mu_B B$ , so  $U$  is zero

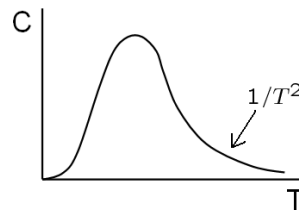


A sketch of  $U$  against  $T$  would look like this.

Now that we know the gradient is zero at both 0 K and high  $T$



we can sketch the heat capacity, which is the gradient of  $U$ .



We have just deduced the Schottky anomaly.

In principle, we can now find the heat capacity  $C$  using

$$C = \frac{dU}{dT}.$$

However, the gradient of  $U$  neat 0 K is not known. We can find this using the Boltzmann distribution.

Near 0 K, nearly all electrons at at the lower state. The very small fraction in the higher state is approximately given by the Boltzmann factor  $\exp(-\varepsilon/k_B T)$  (why?), where

$$\varepsilon = 2\mu_B B.$$

The total energy is then

$$U = -N\mu_B B + N\mu_B \exp(-\varepsilon/k_B T).$$

Differentiating this shows that the gradient goes to zero as  $T$  goes to 0 K.

We shall now use the Boltzmann distribution to derive a formula for  $U$  and  $C$ . There are two levels:

$$\varepsilon_1 = -\mu_B B \text{ and } \varepsilon_2 = +\mu_B B.$$

The total energy is

$$U = \sum n_i \varepsilon_i$$

The number of electrons in level  $i$  is given by

$$n_i = A \exp(-\varepsilon_i/k_B T).$$

We must solve for  $A$  first. The total number is

$$N = A \sum \exp(-\varepsilon_i/k_B T).$$

The sum is called the single particle partition function:

$$Z_{SP} = \sum \exp(-\varepsilon_i/k_B T)$$

Solving for  $A$  gives

$$A = \frac{N}{Z_{SP}}.$$

So

$$n_i = \frac{N}{Z_{SP}} \exp(-\varepsilon_i/k_B T).$$

The total energy is

$$U = \sum n_i \varepsilon_i$$

Substituting  $n_i$ :

$$U = \frac{N}{Z_{SP}} \sum \varepsilon_i \exp(-\varepsilon_i/k_B T).$$

Substituting for  $\varepsilon_i$ :

$$U = \frac{N}{Z_{SP}} [-\mu_B B \exp(\mu_B B/k_B T) + \mu_B B \exp(-\mu_B B/k_B T)].$$

and in  $Z_{SP}$  as well:

$$U = N \frac{-\mu_B B \exp(\mu_B B/k_B T) + \mu_B B \exp(-\mu_B B/k_B T)}{\exp(\mu_B B/k_B T) + \exp(-\mu_B B/k_B T)}$$

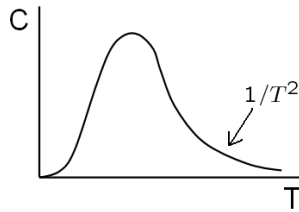
Simplifying, we find  $U$ :

$$U = -N\mu_B B \tanh(\mu_B B/k_B T).$$

Differentiating  $U$  gives the heat capacity:

$$C = Nk_B \left( \frac{\mu_B B}{k_B T} \right)^2 \operatorname{sech}^2 \left( \frac{\mu_B B}{k_B T} \right).$$

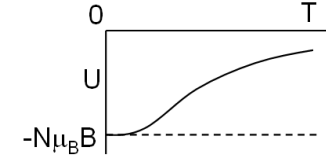
which also gives the Schottky anomaly that we deduced:



The formula

$$U = -N\mu_B B \tanh(\mu_B B/k_B T).$$

does indeed give the graph that we deduced earlier on:



We note here that a useful formula from the above formula for  $n_i$ , is the probability that an electron is at level  $\varepsilon_i$ :

$$p_i = \frac{n_i}{N} = \frac{\exp(-\varepsilon_i/k_B T)}{Z}.$$

The entropy.

We can find the entropy using

$$dS = \frac{dQ}{T} = \frac{dU}{T}.$$

In our case,  $Q$  is just  $U$  since no work is done. So

$$S = \int \frac{dU}{T} = \int \frac{C dT}{T}.$$

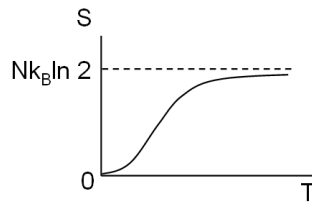
This can be done analytically using the earlier formula for  $C$ .

The result is

$$S = Nk_B \ln \left[ 2 \cosh \left( \frac{\mu_B B}{k_B T} \right) \right] - \frac{N\mu_B B}{T} \tanh \left( \frac{\mu_B B}{k_B T} \right).$$



The graph for the entropy looks like this:



Again, we would be interested in the high and low temperature behaviours.

Recall the formula for entropy:  $S = k_B \ln \Omega$ .

## Ideal Gas

At low temperature, most atoms would be in the ground state.

$$\begin{array}{l} +\mu_B B \text{ ———} \\ -\mu_B B \text{ —}\uparrow\downarrow\text{—} \end{array}$$

There is only 1 way to arrange this. So the entropy would tend to  $S = k_B \ln 1 = 0$ .

At high temperature, the difference between the energy levels would be small compared with the  $k_B T$  in  $\exp(-\epsilon/k_B T)$ .

$$\begin{array}{l} +\mu_B B \text{ —}\uparrow\text{—} \\ -\mu_B B \text{ —}\downarrow\text{—} \end{array}$$

The atom is equally likely to be in either level. There are 2 possible arrangements for each of the  $N$  atoms -  $2^N$  in total.

So the entropy would tend to  $S = k_B \ln 2^N = Nk_B \ln 2$ .

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## A particle in a 3-D box

In an ideal gas, we assume that there is little interaction between atoms.

From the kinetic theory of gases, we know that the average energy of each atom in an ideal gas is

$$\frac{1}{2}mv^2 = \frac{3}{2}k_B T.$$

This means that the total energy is

$$U = \frac{3}{2}Nk_B T$$

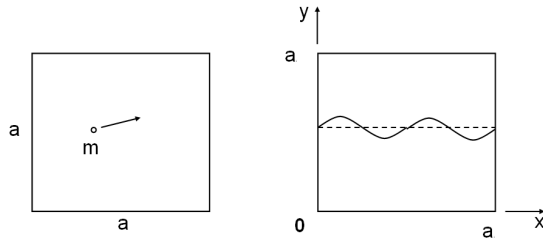
and the heat capacity is

$$C = \frac{dU}{dT} = \frac{3}{2}Nk_B.$$

[http://en.wikipedia.org/wiki/Kinetic\\_theory](http://en.wikipedia.org/wiki/Kinetic_theory)

We shall rederive this here using statistical mechanics. The ideas will also be used for electrons and phonons.

Consider a particle in a 3-D box.



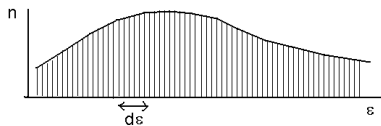
Solving the Schrodinger's equation, we get the same quantisation condition as in the 1D box. For the  $x$  direction,

$$k_x = \frac{n_x \pi}{a}.$$

Likewise for the  $y$  and the  $z$ .

### Density of states.

This suggests that we may approximate the graph to a curve, and the sum to an integral.



Within a small interval  $d\varepsilon$ ,  $n_i$  is nearly constant. Then the sum of the energies of particles is approximately  $n_i \varepsilon_i$  times the number of states in this interval.

If we divide this number of states by  $d\varepsilon$ , we can think of the answer as a kind of density. This density of states (DOS) is often denoted by the function  $g(\varepsilon_i)$ .

The number states in  $d\varepsilon$  is then  $g(\varepsilon)d\varepsilon$ , and the energy in the interval given by  $n_i \varepsilon_i g(\varepsilon_i) d\varepsilon$ .

### Density of states.

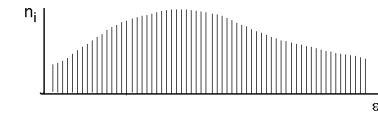
To find the heat capacity of  $N$  particles, we need the energy

$$U = \sum n_i \varepsilon_i.$$

For the spin 1/2 salt, there are only 2 levels to sum. For the particle in the box, there are many levels.

At room temperature, many of these levels could be occupied. This is because for an ideal gas, spacing between energy levels is much smaller than the average energy of a particle. (Prove it.)

As a result, a plot of  $n_i$  against  $\varepsilon_i$  may look like this.



### Density of states.

The total energy

$$U = \sum n_i \varepsilon_i.$$

can be written as

$$U = \sum n_i \varepsilon_i g(\varepsilon_i) d\varepsilon.$$

Approximating this as an integral gives

$$U = \int n(\varepsilon) \varepsilon g(\varepsilon) d\varepsilon.$$

where we have replaced the subscript with the argument  $\varepsilon$ .

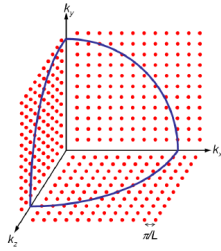
This creates a new problem. We must now find the DOS.

The wavevectors

$$k_x = \frac{n_x \pi}{a}$$

are quantised at uniform intervals in all three directions.

we can imagine a  $k$  space in which the the  $x$  coordinate is  $k_x$ , and so on. If we use a point to represent each state, we would get a lattice like this.



## DOS

We find that the total number of states below  $k$  is

$$G(k) = \frac{V k^3}{6\pi^2},$$

where  $V$  is the volume  $a^3$  of the box.

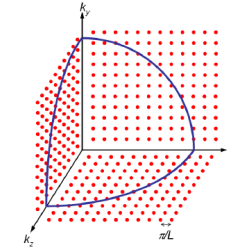
Suppose  $k$  is increased by  $dk$ . Then the number of states increases by  $dG$ . So the density of states is

$$g(k) = \frac{dG(k)}{dk} = \frac{V k^2}{2\pi^2}.$$

We have earlier defined the DOS in terms of energy,  $g(\varepsilon)$ .

Important: To convert the variable to energy, it is not a simple matter of substituting the formula

$$\varepsilon = \frac{\hbar^2 k^2}{2m}.$$



First, we find the number of all states below energy  $\varepsilon$ . This means the number of points within 1/8 (why?) of the sphere of radius  $k$ , where  $k$  is the wavevector for  $\varepsilon$ .

Since the spacing between points is  $\pi/a$ , the volume associated with each point is  $(\pi/a)^3$ . Therefore, the total number of states is:

$$G(k) = \frac{1}{8} \times \frac{4}{3} \pi k^3 \div \left(\frac{\pi}{a}\right)^3.$$

## Changing variables

The reason is that for the same interval  $\varepsilon$ , the size of the interval  $dk$  can be different at different energy because the relation

$$\varepsilon = \frac{\hbar^2 k^2}{2m}$$

is not linear. (Prove it.)

The correct way is to use the method for probability density function:

$$g_\varepsilon(\varepsilon)d\varepsilon = g_k(k)dk.$$

[http://en.wikipedia.org/wiki/Probability\\_density\\_function](http://en.wikipedia.org/wiki/Probability_density_function)

The subscripts are added here to emphasise that  $g(\varepsilon)$  and  $g(k)$  are different functions.

Rearranging,

$$g_\varepsilon(\varepsilon) = g_k(k) \frac{dk}{d\varepsilon}.$$

We can now substitute the relation

$$\varepsilon = \frac{\hbar^2 k^2}{2m}$$

to find  $g_\varepsilon(\varepsilon)$ . The answer is

$$g(\varepsilon) = \frac{4m\pi V}{h^3} (2m\varepsilon)^{1/2}$$

where we have dropped the subscript again, as is the normal practice. (Misleading, but you can tell from the argument.)

For comparison:

$$g(k) = \frac{V k^2}{2\pi^2}.$$

## Ideal gas energy states

In an ideal gas at room temperature, it is very unlikely for two or more atoms to occupy the same energy state. So we can assume that each state is occupied by only one atom. This simplifies the calculation of the macrostate.

First, we should justify the assumption.

At a temperature  $T$ , we know from simple kinetic theory of ideal gas that the average energy of a gas atom is about  $3k_B T/2$ .

We need to know how many energy states there are below this energy at room temperature.

It is also useful to have the formula for total number states

$$G(k) = \frac{1}{8} \times \frac{4}{3} \pi k^3 \div \left(\frac{\pi}{a}\right)^3.$$

in terms of energy.

Since no  $\varepsilon$  or  $k$  intervals are involved, we can simply substitute

$$\varepsilon = \frac{\hbar^2 k^2}{2m}.$$

The answer is

$$G(\varepsilon) = \frac{4\pi V}{3h^3} (2m\varepsilon)^{3/2}.$$

## Ideal gas energy states

We can use the formula we have derived:

$$G(\varepsilon) = \frac{4\pi V}{3h^3} (2m\varepsilon)^{3/2}$$

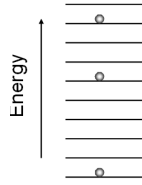
by setting  $\varepsilon = 3k_B T/2$ .

Putting in the numbers for one mole of ideal gas at room temperature, we find that the number of states below  $3k_B T/2$  is about  $10^{30}$ .

1 mole of gas contains about  $10^{24}$  atoms.

This means we have about  $10^{30} \div 10^{24} = 10^6$  states per atom.

This means we have about 1 million energy states for every atom.



So it is extremely unlikely that two atoms would ever occupy the same energy state.

We can use this result to derive the energy distribution of these atoms, with the help of the Lagrange multipliers.

### Macrostate.

Use the method of combinations, we find

$$\frac{(n_i + g_i)!}{n_i! g_i!}$$

possible arrangements.

To find the total number of arrangements for all intervals, we must multiply together the answer for every interval:

$$\Omega = \prod_i \frac{(n_i + g_i)!}{n_i! g_i!}.$$

Since the number of energy states  $g_i$  is much larger than the number of atoms  $n_i$ , we can simplify this to

$$\Omega = \prod_i \frac{g_i^{n_i}}{n_i!}.$$

Consider a interval  $\varepsilon_i$  around the energy  $\varepsilon_i$ . Suppose there are are  $n_i$  atoms and  $g_i$  states in this interval.

We need to find the number of microstates. We cannot do it the same way as in the paramagnetic salt example. This is because the particles in the ideal gas are indistinguishable.

(Although the ions in the salt are identical, they are distinguishable - because of their fixed positions in the solid.)

The problem then is the same as that of arranging  $n_i$  identical balls and  $g_i$  identical partitions in a row.

### Most probable macrostate

We can now apply the Lagrange multiplier method.

The answer is

$$n_i = A g_i \exp(-\varepsilon_i / k_B T),$$

which is the Boltzmann distribution again.

We can find  $A$  using

$$N = \sum n_i.$$

To approximate to an integral as before, recall that the number of states  $g_i$  in the energy interval is given by  $g(\varepsilon)d(\varepsilon)$ .

Then  $n_i$  above becomes

$$n(\varepsilon)d\varepsilon = A g(\varepsilon) \exp(-\varepsilon / k_B T) d\varepsilon,$$

and

$$N = A \int g(\varepsilon) \exp(-\varepsilon / k_B T) d\varepsilon.$$

The integral

$$Z_{SP} = \int g(\epsilon) \exp(-\epsilon/k_B T) d\epsilon.$$

is just continuous energy version of the single particle partition function that we have used earlier (for the spin 1/2 salts):

$$Z_{SP} = \sum \exp(-\epsilon_i/k_B T).$$

So we get the same relation

$$N = AZ_{SP}, \text{ or } A = \frac{N}{Z_{SP}}.$$

Substituting the formula for  $g(\epsilon)$ , we find

$$Z_{SP} = V \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2},$$

$$A = \frac{N}{V} \left( \frac{h^2}{2\pi m k_B T} \right)^{3/2}$$

At the Columbia University in New York,

Miller and Kusch measured the speeds of the atoms in potassium vapour. They agree very well with the formula.

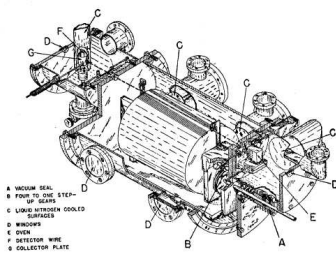


FIG. 2. Schematic diagram of the apparatus designed to measure velocity distributions.

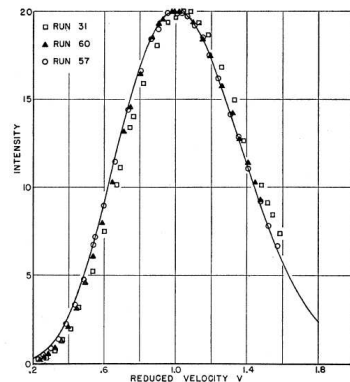


FIG. 4. Typical potassium velocity distributions. The vapor pressures in the ovens are given in Table II. Run 31 was made with thick oven slits and runs 57 and 60 with thin slits.

This was published in Physical Review in 1955.

and

$$n(\epsilon) = \frac{2\pi N}{(\pi k_B T)^{3/2}} (\epsilon)^{1/2} \exp(-\epsilon/k_B T).$$

The energy is just the kinetic energy,  $\epsilon = mv^2/2$ . We can change to variable  $v$  using

$$n(v)dv = n(\epsilon)d\epsilon.$$

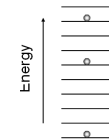
This gives the velocity distribution

$$n(v) = N \left( \frac{2}{\pi} \right)^{1/2} \left( \frac{m}{k_B T} \right)^{3/2} \exp(-mv^2/2k_B T) v^2$$

This is the Maxwell-Boltzmann distribution.

When would it break down?

We have assumed that: "It is extremely unlikely that two atoms would ever occupy the same energy state."



Recall that we have arrived at this by looking at the number of states below the mean energy  $3k_B T/2$ , when  $T$  is at room temperature.

If  $T$  is very small, there may be far fewer states below the mean energy. Then it would be very likely for two atoms to occupy the same state, and the Maxwell-Boltzmann distribution would not be valid.

Instead, quantum statistics - such as Fermi-Dirac or Bose-Einstein - have to be used. We shall learn about this.

That there is a set of formulae that we can use to find the energy from the partition function.

The energy is given by:

$$U = k_B T^2 \frac{\partial \ln Z_N}{\partial T}$$

where the many particle partition function  $Z_N$  for indistinguishable particles is

$$Z_N = \frac{Z_{SP}^N}{N!}.$$

(Prove it.)

Substituting this, we find

$$U = \frac{3Nk_B T}{2} \text{ and } C = \frac{dU}{dT} = \frac{3}{2} Nk_B,$$

as expected from kinetic theory.

## Exercises

Recall that the Boltzmann distribution comes from Boltzmann's postulate

$$S = k_B \ln \Omega.$$

The ability to derive the correct heat capacities for paramagnetic salts, ideal gases, and other systems are strong evidence that the postulate is correct.

Results such as the heat capacity

$$C = \frac{3}{2} Nk_B$$

can be directly measured on real gases that are nearly ideal, such as Helium.

This provides a means to obtain the Boltzmann constant, which turns out to be related to the gas constant:

$$k_B = \frac{R}{N_A}.$$

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## Some exercises

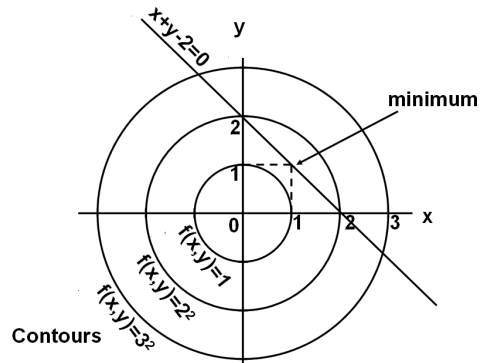
### Exercise 1

Minimise the function  $f(x, y) = x^2 + y^2$ , subject to the constraint  $x + y - 2 = 0$ .

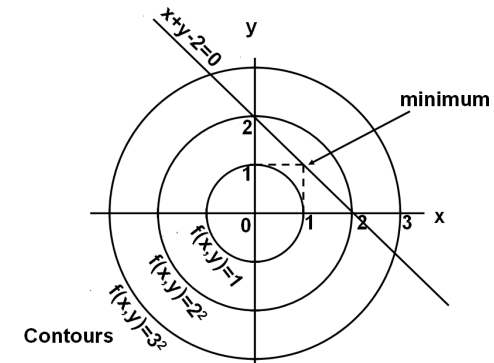
(i) Do it mentally, or by inspection of the graphs.

(ii) Do it using Lagrange multiplier.

Do the results agree?



1. The contours of  $f(x, y)$  are just circles, e.g.  $x^2 + y^2 = 1$ ,  $x^2 + y^2 = 2$ , ... The circles get larger as the value increases.
2. The constraint  $x + y - 2 = 0$  is a straight line with intercepts  $x = 2$  or  $y = 2$ .



1. By symmetry,  $f(x, y)$  is highest at the midpoint between the intercepts, where  $x = y = 1$ .
2. Therefore,  $f(x, y) = 1^2 + 1^2 = 2$ .

1. Let  $g(x, y) = x + y - 2$ . The constraint is then  $g(x, y) = 0$ .
2. The Lagrange function is

$$f(x, y) + \lambda g(x, y) = x^2 + y^2 + \lambda(x + y - 2) \quad (1)$$

3. The gradient gives:
  1. Differentiate wrt  $x$ :  $2x + \lambda = 0$ .
  2. Differentiate wrt  $y$ :  $2y + \lambda = 0$ .
4. Solving with the constraint equation gives  $\lambda = -2$  and  $x = y = 1$ , as before.

## Exercise 2

Use your calculator to work out  $\ln 10!$ . Compare your answer with the simple version of Stirling's theorem ( $N \ln N - N$ ). How big must  $N$  be for the simple version of Stirling's theorem to be correct to within (ii) 5% (ii) 1% ?

## Answer

$\ln(10!) = 15.11$  whereas  $10 \ln(10) - 10 = 13.03$ . There is less than 5% difference for  $N = 24$  and less than 1% for  $N = 91$ . Stirling's approximation is quite accurate even for relatively small  $N$ .



**Exercise 3**

Consider a 10000 distinguishable particles at room temperature, 298 K. Suppose that each particle has 2 energy levels, 0.01 eV and 0.02 eV. Find the number of the particles in each energy level. ( Boltzmann's constant is  $1.3807 \times 10^{-23} \text{ J K}^{-1}$ .)

---

**Exercise 4****Exercise 4**

Calculate the quantity  $k_B T$  at room temperature, 298 K. Give the answer in eV. ( Boltzmann's constant is  $1.3807 \times 10^{-23} \text{ J K}^{-1}$ . Electron charge is  $1.6 \times 10^{-19} \text{ C}$ .)

**Answer**

In Joules,  $k_B T = 1.3807 \times 10^{-23} \times 298 = 4.114 \times 10^{-21} \text{ J}$ .

In eV,  $k_B T/e = 4.114 \times 10^{-21}/1.6 \times 10^{-19} = 0.026 \text{ eV}$ .

Note: Since  $1/40 = 0.025$  is quite close to this answer,  $k_B T$  at room temperature is often quoted as  $1/40 \text{ eV}$ .

**Answer**

Since the number is quite large, we assume that the probability at each energy level is given by Boltzmann's distribution  $A \exp(-\varepsilon/k_B T)$ .

At 0.01 eV,  $A \exp(-\varepsilon/k_B T) = 0.6778A$ .

At 0.02 eV,  $A \exp(-\varepsilon/k_B T) = 0.4594A$ .

The total is  $0.6778A + 0.4594A = 10000$ . So  $A = 8794$ .

Therefore the numbers are:

at 0.01eV,  $0.6778 \times 8794 = 5961$ ;

at 0.02eV,  $0.4594 \times 8794 = 4040$ .

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**Exercise 5****Exercise 5**

Consider a large number of distinguishable particles, at temperature  $T$ . Each particle has 4 energy levels 0,  $k_B T$ ,  $2k_B T$  and  $3k_B T$ . Calculate the fraction of particles in each energy level.

**Answer**

Since the number is quite large, we assume that the probability at each energy level is given by Boltzmann's distribution  $A \exp(-\varepsilon/k_B T)$ .

First, calculate the following:

at energy 0,  $\exp(-\varepsilon/k_B T) = \exp(0) = 1$ .

at energy  $k_B T$ ,  $\exp(-\varepsilon/k_B T) = \exp(-1) = 0.3679$ .

at energy  $2k_B T$ ,  $\exp(-\varepsilon/k_B T) = \exp(-2) = 0.1353$ .

at energy  $3k_B T$ ,  $\exp(-\varepsilon/k_B T) = \exp(-3) = 0.0498$ .

The sum is 1.553. The fractions are, therefore:

at energy 0,  $1/1.553 = 0.6439$ .

at energy  $k_B T$ ,  $0.3679/1.553 = 0.2369$ .

at energy  $2k_B T$ ,  $0.1353/1.553 = 0.0871$ .

at energy  $3k_B T$ ,  $0.0498/1.553 = 0.0321$ .

Notice that fraction drops to nearly 1/10 after just  $2k_B T$ .

In statistical mechanics, we often want to know if an energy level is likely to be populated at some temperature. If the level is much higher than  $k_B T$ , then it is unlikely to be occupied.

## Some exercises

## Answer

First, note that since  $Z = \sum \exp(-\varepsilon_i/k_B T)$

$$N = A \sum_i \exp(-\varepsilon_i/k_B T) = AZ$$

Next,

$$\frac{\partial \ln Z}{\partial T} = \frac{1}{Z} \frac{\partial Z}{\partial T} = \frac{1}{Z} \sum \frac{\varepsilon_i}{k_B T^2} \exp(-\varepsilon_i/k_B T)$$

Multiplying the two equations above,

$$N \frac{\partial \ln Z}{\partial T} = \frac{A}{k_B T^2} \sum \varepsilon_i \exp(-\varepsilon_i/k_B T)$$

## Exercise 6

Given that the total energy of a system is

$$U = A \sum_i \varepsilon_i \exp(-\varepsilon_i/k_B T)$$

where  $A$  is defined by the normalisation from

$$N = A \sum_i \exp(-\varepsilon_i/k_B T)$$

demonstrate that

$$U = N k_B T^2 \frac{\partial \ln Z}{\partial T}$$

where

$$Z = \sum_i \exp(-\varepsilon_i/k_B T)$$

## Some exercises

Rearranging,

$$N k_B T^2 \frac{\partial \ln Z}{\partial T} = A \sum \varepsilon_i \exp(-\varepsilon_i/k_B T)$$

which is  $U$ . Therefore

$$N k_B T^2 \frac{\partial \ln Z}{\partial T} = U$$

**Exercise 7**

The total energy of a paramagnet is

$$U = -N\mu_B B \tanh(\mu_B B/k_B T)$$

Show that the heat capacity is given by

$$C = Nk_B \left(\frac{\theta}{T}\right)^2 \frac{\exp(\theta/T)}{(\exp(\theta/T) + 1)^2}$$

where  $\theta = 2\mu_B B/k_B$

Show that the limiting form at high temperature is

$$C = \frac{Nk_B}{4} \left(\frac{\theta}{T}\right)^2$$

and at low temperature is

$$C = Nk_B \left(\frac{\theta}{T}\right)^2 \exp(-\theta/T)$$

At high temperature,  $\exp(\theta/T) \rightarrow 1$ .

$$\begin{aligned} C &= Nk_B \left(\frac{\theta}{T}\right)^2 \frac{\exp(\theta/T)}{(\exp(\theta/T) + 1)^2} \\ &\rightarrow Nk_B \left(\frac{\theta}{T}\right)^2 \frac{1}{(1 + 1)^2} \\ &= \frac{Nk_B}{4} \left(\frac{\theta}{T}\right)^2 \end{aligned}$$

At low temperature,  $\exp(\theta/T) + 1 \rightarrow \exp(\theta/T)$ .

$$\begin{aligned} C &= Nk_B \left(\frac{\theta}{T}\right)^2 \frac{\exp(\theta/T)}{(\exp(\theta/T) + 1)^2} \\ &\rightarrow \left(\frac{\theta}{T}\right)^2 \frac{\exp(\theta/T)}{\exp(\theta/T)^2} \\ &= Nk_B \left(\frac{\theta}{T}\right)^2 \exp(-\theta/T) \end{aligned}$$

**Answer**

The heat capacity is obtained by differentiating

$$U = -N\mu_B B \tanh(\mu_B B/k_B T):$$

$$C = \frac{dU}{dT} = -N\mu_B B \left(\frac{-\mu_B B}{k_B T^2}\right) \left[\cosh\left(\frac{\mu_B B}{k_B T}\right)\right]^{-2}$$

In terms of  $\theta = 2\mu_B B/k_B$ ,

$$\begin{aligned} C &= Nk_B \left(\frac{\theta}{2T}\right)^2 \left[\cosh\left(\frac{\theta}{T}\right)\right]^{-2} \\ &= Nk_B \left(\frac{\theta}{2T}\right)^2 \frac{4}{(\exp(\theta/2T) + \exp(-\theta/2T))^2} \\ &= Nk_B \left(\frac{\theta}{T}\right)^2 \frac{1}{(\exp(\theta/2T) + \exp(-\theta/2T))^2} \cdot \frac{\exp(\theta/T)}{\exp(\theta/T)} \\ &= Nk_B \left(\frac{\theta}{T}\right)^2 \frac{\exp(\theta/T)}{(\exp(\theta/T) + 1)^2} \end{aligned}$$

**Exercise 8**

Show that the partition function of an ideal gas:

$$Z = \int_0^\infty \frac{4m\pi V}{h^3} (2m\varepsilon)^{1/2} \exp(-\varepsilon/k_B T) d\varepsilon$$

is given by:

$$Z = V \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}.$$

[You are given that

$$\int_{-\infty}^\infty x^{2n} e^{-a^2 x^2} dx = \frac{(2n)! \pi^{1/2}}{n! (2a)^{2n} a}$$

]

---

First, move the constant factors outside the integral:

$$Z = \frac{4m\pi V}{h^3} (2m)^{1/2} \int_0^\infty \varepsilon^{1/2} \exp(-\varepsilon/k_B T) d\varepsilon$$

There is no power of 1/2 in the integration formula that is given. So we start with the substitution

$$\varepsilon = x^2$$

Then

$$\begin{aligned} Z &= \frac{4m\pi V}{h^3} (2m)^{1/2} \int_0^\infty x \exp(-x^2/k_B T) \cdot 2x dx \\ &= \frac{4m\pi V}{h^3} (2m)^{1/2} 2 \int_0^\infty x^2 \exp(-x^2/k_B T) dx \end{aligned}$$

Next, set  $n$  to 1 in the given formula:

$$\int_{-\infty}^\infty x^2 e^{-a^2 x^2} dx = \frac{2\pi^{1/2}}{(2a)^2 a}$$

The lower limit of this integral is  $-\infty$ . To make this agree with the integral for the partition function  $Z$  ...

We get

$$Z = \frac{4m\pi V}{h^3} (2m)^{1/2} 2 \frac{\pi^{1/2}}{4} (k_B T)^{3/2}$$

Simplifying,

$$Z = V \left( \frac{2m\pi k_B T}{h^2} \right)^{3/2}$$

we get the formula for the partition function.

We change the lower limit to 0 and halve the right hand side, and the formula becomes:

$$\int_0^\infty x^2 e^{-a^2 x^2} dx = \frac{\pi^{1/2}}{(2a)^2 a}$$

Now comparing with the partition function again:

$$Z = \frac{4m\pi V}{h^3} (2m)^{1/2} 2 \int_0^\infty x^2 \exp(-x^2/k_B T) dx$$

the integrals become the same if we set

$$a^2 = \frac{1}{k_B T}.$$

Substituting this into the formula gives

$$\int_0^\infty x^2 e^{-x^2/k_B T} dx = \frac{\pi^{1/2}}{4} (k_B T)^{3/2}$$

Substituting this into partition function integral, ...

## Exercise 9

What is the root-mean-square speed of a helium atom at room temperature?

[Given that the relative atomic mass of helium is 4.

Atomic mass unit  $u$  is  $1.6605 \times 10^{-27}$  kg.

Boltzmann's constant  $k_B$  is  $1.3807 \times 10^{-23}$  J K<sup>-1</sup>. ]

---

First, we find the mean of  $v^2$ . This is can be obtained by

$$\bar{v^2} = \frac{1}{N} \int_0^\infty v^2 n(\varepsilon) d\varepsilon.$$

We have multiplied  $v^2$  by the number particles at each energy interval  $d\varepsilon$ , and divided by the total number  $N$ .

The energy of the atom in an ideal gas is just the kinetic energy,

$$\varepsilon = \frac{1}{2}mv^2.$$

If we rewrite the above integral for  $v^2$  in terms of the energy, we get

$$\bar{v^2} = \frac{2}{Nm} \int_0^\infty \varepsilon n(\varepsilon) d\varepsilon.$$

This integral is just the total energy  $U$ , i.e.

$$\bar{v^2} = \frac{2}{Nm} U.$$


---

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We can now calculate the root-mean-square speed. The mass of the helium atom is

$$4u = 4 \times 1.6605 \times 10^{-27} = 6.642 \times 10^{-27} \text{ kg}.$$

Taking the room temperature as 298 K, the answer is

$$\begin{aligned} \sqrt{\bar{v^2}} &= \sqrt{\frac{3k_B T}{m}} \\ &= \sqrt{\frac{3 \times 1.3807 \times 10^{-23} \times 298}{6.642 \times 10^{-27}}} \\ &= 1363 \text{ m/s} \end{aligned}$$

---

We have previously obtained the energy  $U$  from the partition function:

$$U = \frac{3}{2} N k_B T.$$

So the mean square speed is

$$\bar{v^2} = \frac{2}{Nm} \frac{3}{2} N k_B T = \frac{3k_B T}{m}$$

The root-mean-square speed is then

$$\sqrt{\bar{v^2}} = \sqrt{\frac{3k_B T}{m}}.$$


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